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⑭ 複写装置

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図面の簡単な説明

第1図は本発明複写装置の1実施例の斜視図、
第2図は第1図の2-2線に沿う拡大断面図、第
3図、第4図および第5図は第2図のそれぞれ
3-3線、4-4線および5-5線に沿う断面図
第6図および第7図は第4図のそれぞれ6-6線
および7-7線に沿う拡大断面図、第8図は第1
図の複写装置の電気配線図である。

発明の詳細な説明

本発明は、タイプライタまたはその他の方法で
書いた材料または印刷した材料、写真、製図、ト
レース、スケッチおよび記録等のような模倣材料
の複写法、殊に感光複写シートに複写を行う複写
装置に関する。

特に本発明は、紫外線の作用に露出したときに
ジアゾ化合物が分解し無色のかつ硬になつても実
質的に無色のまゝになつてゐる物質を生成する現
象とさらにジアゾ化合物がまた別の実質的に無色

の発色剤と呼ぶ物質と化合して光線に感じないで
恒久的な可視像を生成できる強いナフトール染料
を生ずる現象とにともづいた方法により複写を行
う複写装置を電氣的に駆動制御する装置に係わる。

本発明は、複写しようとする原板から直接、こ
の複写しようとする原板とこれに重ね合わせた感
光複写シートとから成る露光サンドイッチ状態を
形成し次でこのサンドイッチ状態を普通の水銀蒸
気灯または紫外線を含むその他の光源により放出
するような紫外線を含む放射線に露光するだけで
模倣材料のジアゾタイプ複写を迅速に行う方法に
使われる。本方法によれば光線は複写シート状態
に原板を介して当てることにより、複写しようと
する模倣材料に対応しこの模倣材料によりしやへ
いした区域を除いた全部分に於て複写シート状態
の感光物質を不活性にする。この露光した複写シ
ート状態は次で加熱しこのようなしやへいした区
域に於て染料生成反応を生じさせてこの複写シ
ート状態に原板の模倣材料の可視複写を現象する。

本発明によれば複写操作に於て、複写しようとする
原板を介して複写シート状態を光源に經次的に
露光し次でこの複写シート状態を液状現像液質内
に浸さなければならない従来の複写法に通常伴う
時間遅れや不便を全く除くことができる。

本発明の主な目的は、模倣材料の複写を行うの
に現像液を使わなくてもよいようにしようとする
にある。さらに本発明の目的は、感光複写シート
状態を複写しようとする原板を介してこのシート
状態に当てる紫外線の作用に露光しこの複写シ
ート状態を加熱しこのシート状態を印面として現像
するだけで複写を現象するための有効な電氣的駆
動ならびに制御装置を提供しようとするにある。

本発明の他の目的は、紫外線に透明なガラスの
ような材料から成る回転自在なスリーブ部片をこ
のスリーブ部片の周面を囲む彎曲部分を持つたわ
み性ベルト部片と協働させて使い複写しようとし
る原板と感光複写シート状態とから成る露光サン

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ドインツ状態を紫外線源を過ぎて移動させるようにした前記のような複写装置を提供しようとするにある。さらに本発明の目的は、前記スリーブ部片内にこれと同軸に配置した普通の管状の紫外線灯を光源として使うようにするにある。

本発明の他の目的は、アルミニウムのような材料から成り紫外線を放射できる回転自在なスリーブ部片を持つシート状体加熱装置をシート状体現像に必要な所望のシート状体加熱時間中に加熱しようとするシート状体を前記スリーブ部片に当てようとするシート状体を前記スリーブ部片に当てようとする保持装置と駆動させて備えた、熱により模様複写を行うシート状体現像装置を提供しようとするにある。さらに本発明の目的は、スリーブ部片の周辺部をこのスリーブ部片の内周方向に於て互に間隔を隔てたシート状体受入れ場所およびシート状体放出場所の間で囲みこのスリーブ部片周辺部に弾性的に連関する彎曲部分を形成する部分を持つベルト部片または幅状体を使うようにするにある。さらに本発明の目的は、現像熱をベルト部片およびこれに向き合うスリーブ部片表面によりこれ等両者間に形成した現像区域に現像熱を保持するように前記ベルト部片の外側に比較的厚い熱絶材層を設けようとするにある。なお本発明の目的は、光線吸収用シート状体加熱スリーブ部片をこのスリーブ部片内にこれと同軸に配置した普通の管状の紫外線灯により加熱しようとするにある。

本発明の他の目的は、サンドイッチ状体成分分離装置内に所望の真空状態を保持する排出装置を提供し、露光区域を換気してこの露光区域を感光性複写シート状体を含むサンドイッチ状体が露光区域を通過する際にこの複写シート状体が現像されないように充分低い温度単位に確実に保つようにする換気装置を提供し、現像区域を精密な制限内で適当な現像温度に保つ制御装置を提供し、露光区域の紫外線灯と現像区域を付勢する紫外線灯との動作を調整し駆動原動機を制御する電気制御回路を提供しようとするにある。

以下本発明複写装置の実施例を図面について詳細に説明する。

図示のように本発明による複写装置Aは、たとえ紙やその他適当な材料から成り紫外線を含む放射線に露光すると安定な無色の状態にある感光性組成物を被覆した幅状体から成る感光シート状体に模様材料を複写することができる。前記組成

物はまた300°F程度の温度に於て熱にさらすと極めてよく見える不活性の安定な状態になる。感光性被覆は、前記の特性を持つ任意適当な物質を使えばよいがジアン化合物およびジアン染料発色剤と共に300°F程度の温度に加熱したときにアルカリ性ジアン染料生成反応を生ずる原薬のような物質を使うのがよい。

原板表面に印刷またはその他の方法で設けた模様または記号を持つ原板の複写を行う際に本発明によれば感光複写シート状体に原板をその後面が複写シート状体の感光層支持面に当たるようにして互に重ね合わせるにより露光サンドイッチ状体を形成する。この露光サンドイッチ状体は次で放射線が複写シート状体の感光材料に原板を介して当たるようにして紫外線的作用にさらすことにより複写シート状体の感光材料の全部を複写しようとする模様材料に対応しかつこの模様材料によりしやへいたシート状体区域に在る部分を除いて不活性にする。この場合このようなしやへいた区域に残っている変性してない感光材料は複写しようとする模様材料の潜像を生成する。これ等の潜像はこのように露光した複写シート状体に加える熱に感応して不活性を極めてよく見える状態に現像するようにしてある。紫外線的作用に対するサンドイッチ状体の露光後に各サンドイッチ状体成分は互に分離し露光した複写シート状体に感光材料を現像するのに充分高い温度に於て熱的作用を及ぼし複写シート状体のしやへいた区域に潜像を生成する。

このために本複写装置は、底板Bと底板Bに支えた互に間隔を隔てた側板P・Pとを持つ主わくFを備えている。本複写装置は、主わくFに取付けられかつこの主わくに支えられた器具を持ち主わくF上に露光区域FZと現像区域DZと露光サンドイッチ状体を露光区域FZ内に送込みこのサンドイッチ状体を露光区域FZを通り次でサンドイッチ状体成分分離装置Sに移動させるシート状体受入れ運搬兼放出装置とを形成してある。このシート状体運搬装置は分離装置Sと協働して本複写装置からサンドイッチ状体の原板成分を放出するように作用すると共に露光した感光シート状体成分を現像区域DZにまた現像区域DZを経て次で本複写装置から仕上りの複写として送出す。

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本複写装置には基板金から成り主わくFに本複写装置の作動部品を囲む位置に於て支えた適当なハウジングGを設けるのがよい。ハウジングGは、主わくFおよび底板Bを取付けた床部分Kと、床部分Kに取付けられ床部分Kの上方に延びる前壁Wと、ヒンジ部片Hにより床部分Kの後縁部にこれに沿つて枢着した枢動カバー部片Cとを備えるのがよい。カバー部片Cは、本複写装置の後部、頂部および両側部を閉じるようにした後壁R、頂壁Tおよび垂下する側壁Sとを備え込んだ複写機10の構造を検査、修理、交換または調整のために容易に操作できるようにしてある。ハウジングGにはまた、前壁Wに露光サンドイッチ状体を露光区域EZを形成する装置部分に導入し露光する入口みぞ穴INと通常前壁Wに入口みぞ穴INの上方に形成され複写しようとする原板を本複写装置から放出する送出し穴OMと頂壁Tに形成され仕上りの複写を本複写装置から放出する送出しみぞ穴OCとから成る適当な入口穴および出口穴を形成してある。

ハウジングGの前壁Wにはまた入口みぞ穴INの前方にみぞ穴INに通ずる扁平な横方向に延びるたな部片ISを形成し露光サンドイッチ状体を入口みぞ穴IN内にこれを経て送出しやすくしてある。たな部片ISおよびみぞ穴INは本複写装置の前方にサンドイッチ状体の原板成分をこのサンドイッチ状体が露光区域EZを横切つた後放出する穴OMの下方に配置するのがよい。ハウジングGにはまた枢着したカバー部片Cの頂壁Tの後部部分に送出し穴OCを経て放出する仕上りの複写印画を受ける位置に於て扁平な上向きの横方向に延びるとい部分Xを形成するのがよい。送出し穴OCは後方に傾斜した向きに於てカバー部片Cの頂壁を貫いて開口する印画案内みぞの放出口を構成し仕上り印画をサンドイッチ状体入口みぞ穴INとまたサンドイッチ状体の原板成分を放出する穴OMとから離れたとい部分Xに放出するようにしてある。カバー部片Cを主わくFに対して閉じた位置に取付けるために適当な掛け金を設けてあるのはもちろんである。

露光区域EZを形成する装置部分は、ハウジングG内で軸線のまわりに回転運動するように主わくFに支えた管状スリーブ部片21により構成してある。スリーブ部片21は素外縁に透明なガラ

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ス、プラスチック材またはその他の材料で作るのがよい。スリーブ部片21は任意適当にまたは好適とする方法で或は適宜に回転運動するように支えてある。細長い管状に形成され両端部に接続電極部片23を持つ電動性素外縁放出灯UVをスリーブ部片21内にこれと同軸に整合するように支えてある。図示のように放出灯UVの両端部は主わくFの側板Pに取付けたブラケット部片25で支えてある。前記両端部はブラケット部片25内にたとえ取付用つる巻ばね部片27により弾性的に取付けるのがよい。電動機28(第4図)により駆動する冷空気を送風機ABは主わく側板Pにスリーブ部片21の一端部からこのスリーブ部片を経て空気を送る位置に於て取付けてある。ハウジング側壁Sには冷却空気をハウジングGに出入させるように通風よろい窓Lを設けてある。

現像区域DZとサンドイッチ状体成分分離装置SSとこれ等に駆動するシート状体移動装置とを備えた本複写装置は露光区域EZの上方に主わく側板P内に形成したブッシュ部片55内に支えたピン部片53により形成した軸線のまわりに揺動運動するように取付けた架わく部片SAに取付けた副装置を設けるのがよい。架わく部片SAは、なるべくはフォアマイカ(Formica(商品名))またはその他の耐熱性材料から成る互に間隔を隔てた1対の板部片57, 59から成っている。板部片57, 59はたとえば板部片57, 59の間に延びこれ等の板部片に対向端部を取付けた支持兼隔離用の棒部片61により互に間隔を隔てて互に固定してある。また両板部片57, 59の間には細長い1対の真空室63, 65が延びそれぞれ対向端部を各板部片57, 59に取付けてある。各真空室63, 65は通常両板部片57, 59の間に横方向に延びる位置に於て互に平行にかつわずかな間隔を隔てて配置した押しアルミニウム管で構成してある。副装置架わく部片SAの一方の側に於て管状の真空室63, 65の開いた端部を側板部片59の内面に密着させたたとえば側板部片59を貫通し真空室63, 65の端部に形成した穴68内にねじ込んだ適当な締付けねじ部片67により側板部片59の内面に密封すると共に締付けてある。各真空室63, 65はそれぞれの対向端部が板部片57の穴を貫いて延び板部片57の外側に開口し吸入ボ

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ンブすなわち送風機S B (第5図)に連結するよう
にしてある。送風機S Bは板部片57の外面に
取付けられ送風機S Bの吸込側が管状部分の開い
た端部を囲んで包みかつこれ等の端部に連通する
ようにしてある。この場合適当な取付ブラケット
部片69, 70を使い真空室83, 85の突出端
部を板部片57に固定するようにしてある。また
送風機S Bを駆動するように電動機71を設けて
ある。

現像区域D Zを形成するシート状体現像装置部
分は相対的に可動な1対のシート状体室内兼移動
用部品94, 95を備えている。複写シート状体
が両部品94, 95間をシート状体受入れ場所
83 (第6, 7図)からこれら部品の円周方向に
於て受入れ場所83から間隔を隔てた送出し場所
84 (第7図)まで移動する際
に複写シート状体に現像熱を与える状態にするよ
うに前記両部品94, 95の少くとも一方を加熱
する加熱部片を設けてある。このために図示のよ
うにアルミニウムまたはその他の適当な熱伝導材
料から成る連続的に回転する円筒形スリーブとし
て形成した部品94の加熱用部片を設けてある。
また部品95は部品94形成するスリーブ部片の
周面にこれを囲むように延設する彎曲部を形成す
る材料から成る帯状体すなわち幅状体により構成
してある。

ジエネラル・エレクトリック・カムパニ
(General Electric Company)製の
2400°Kの呈色温度定格を持つT-3号の管状石英
灯である。スリーブ部片119は銅のような導電
性材料から構成してある。スリーブ部片119は
電気および熱の絶縁性材料から成るカバー部片
113内に支えてあるからスリーブ部片119は
赤外線灯I Rの電子フェルール部片を赤外線灯
I Rに付勢電力を送出するための外部の電気回路に
電気的に接続する作用をする。赤外線灯支持スリ
ーブ部片119の1つには赤外線灯I Rを取付位
置にびつたり取付けるように赤外線灯I Rの端部
に弾性的に押付けるばね部片を設けるのがよい。

なるべくサーミスタ147を形成する材料か
ら成る小片で構成した感熱部片を幅状体部品95
内に受入れ場所83および送出し場所84の間に
つねにスリーブ状部品94の表面の温度に感ずる
場所に埋込んである(第6図)。従つてサーミ

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スタ147は赤外線灯I Rへの動作エネルギーの供給
を制御する監視部片として作用させ感熱シート材
料が受入れ場所83から送出し場所84までスリ
ーブ状部品94の外周と熱交換しながら移動する
際にこの感熱シート材料に熱を加える動作温度を
精密に限度内に保つようにしてある。サーミスタ
147は平らな面を一方の側に形成した球面体と
して形成するのがよい。この球面体は幅状体部品
95の穴内にサーミスタ147の平らな面がスリ
ーブ状部品94に純粋テフロン製の幅状体部品から
離れた面に向き合つて連関するようにして取付け
てある。従つてサーミスタ147の平らな側面は
感熱材料から成るシート状体をスリーブ状部品
94のまわりにスリーブ状部品94と幅状体部品
95との間を通つてシート状体受入れ場所83か
らシート状体送出し場所84まで運ぶ際に前記シ
ート状体に熱が加わるのと全く同じ温度で幅状体
に於て内部部品95へ送り出される熱にさらされる
位置になる。サーミスタ147は、これに接続さ
れこれから赤外線灯I Rの動作を調整するよう
にした外部の制御回路まで延びる導線を備えている
のはもちろんである。

第8図に明らかなように本複写装置は給電線
L-1, L-2を接続した任意適当な電源から付
勢できる。給電線L-1, L-2は本複写装置に
分配導線225, 225'を接続した適当な過負荷
電路しや断部片223を介して接続してある。駆
動電動機199は分配導線225, 225'の間に
親スイッチ部片227および速度制御部228で
制御するように電気的に接続してある。制御部
228は通常、調整自在な抵抗器229により定
まる印加電圧を変えることにより電動機199の
速度を制御するように動作する型式番号
367507AA112B1のスタトロール(Statot
rol)商品名)のようなゼネラル・エレクトリッ
ク・カムパニ(General Electric Company)
製の装置を使つてある。

現像区域D Zのスリーブ状部品94を加熱する
加熱部片となる赤外線灯I Rは親スイッチ部片
227を閉じたときに刃部片230, 230'を持
つ通常は開いたなるべく二極のスイッチ部片
CSの制御のもとに分配導線225, 225'か
ら付勢する。刃部片230, 230'は傾板Pの
一方にカバー部片Cを閉位置に傾斜したときにカ

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バー部片Cにより閉じられる位置に取付けられこの閉じた位置に保持される。従つて赤外線灯IRはカバー部片Cを閉じなければ付勢されない。親スイッチ部片227およびカバー部片Cが閉じた位置に在るときは赤外線灯IRは駆動ソレノイド233を持つ継電器スイッチ部片232の制御のもとに動作するよう電線231, 231'を介して付勢する。ソレノイド233を熱応答サーミスタ147の制御のもとにヒスリーブ状部品94の温度に応じて赤外線灯IRを選択的に付勢するように普通の増幅器235を設けてある。増幅器235は通常フエンワール・インコーポレーテッド (Fenwal Inc.) 製の型式番号535の温度制御器のような装置を使つてある。増幅器235はスイッチ部片227, C8を介して閉じたときに付勢され電線149によりサーミスタ147を制御作用を伴うように接続してある。

継電器スイッチ部片232の駆動ソレノイド233はこのソレノイドを図示のように増幅器235の出力側に電線231, 231'の間に直列に接続することにより増幅器235の制御のもとに付勢する。増幅器235の動作特性はこれに電氣的に接続した遅延電位差計〔抵抗器237, 238, 239から成る〕を調整することにより変えられスイッチ部片232をサーミスタ147により定まる増幅器235の動作範囲内で任意所望の温度単位に於て開閉させるようにできる。このようにして電位差計の抵抗器237, 239は互に連結され熱現像部の温度単位を±50°Fの範囲内で保持するように抵抗器238が動作する温度データを定めるように調整できる。また温度調整用のこの電位差計は速度制御抵抗器229と連動させる(図示してない)のが普通である。そうすれば現像区域の動作温度はこの現像区域を通る処理しようとするシートの移動速度の調整と同時

に調整することができる。温度制御器すなわち増幅器235とこれに協働するサーミスタ147と調整自在な電位差計とは感熱材料を現像部の受入れ場所83(第8, 7図)および送出し場所84(第11図)の間に運ぶ際この感熱材料を処理するように加える熱の所望の温度単位を精密かつ正確に保つことができる。前記した温度制御器等は温度単位を精密な所望温度単位の下上5°Fの範囲内に制御できるばかりで

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なく壁厚の薄い金属製加熱円筒部片内に加熱源として赤外線灯を連結したときに極めて早く応答する。サーミスタ147を前記したようにしてベルト状部品95に取付けるときはサーミスタ147の感度を処理シートに熱を加える温度を定める際に最適な効率を持つようにすることができる。

また本発明はスイッチ部片227, C8の制御のもとに動作する紫外線灯UVを付勢する付勢装置に係わる。このために紫外線UVは、変圧器240の2次巻線と34F程度の容量を持つコンデンサに並列の比較的高い値を持つ漏れ抵抗を備えた抵抗コンデンサ回路網241とに直列に接続してある。変圧器240の1次側は紫外線灯冷却送風機電動機28と同様に継電器242, 243の制御のもとに電源から付勢する。各継電器242, 243はそれぞれスイッチ部片駆動コイルすなわちソレノイド242', 243'と双投スイッチ部片とを備えている。図示のように継電器242は刃部片Ax, Bx, Cxと刃部片Axが交互に接触する協働接点a, a'と刃部片Bxが交互に電氣的に接触する協働接点b, b'と刃部片Cxが交互に電氣的に接触する協働接点c, c'を持つ双投3極スイッチを備えている。

継電器243は、刃部片Dx, Exと刃部片Dxが交互に電氣的に接触する協働接点d, d'と刃部片Exが交互に電氣的に接触する協働接点e, e'を持つ双投2極スイッチを備えている。刃部片Ax, Bx, Cx, Dx, Exは通常それぞれ、継電器の動作ソレノイド242', 243'が消勢したままになつている限りは接点a, b, c, d, eに電氣的に接続している。継電器のスイッチ刃部片は各継電器のソレノイドが付勢されたときはつねにまた付勢されたままになつている限りはそれぞれ接点a, b, cと接点d, eとの電氣的接続をしや断しまたそれぞれ接点a', b', c'と接点d', e'とに接続している。

継電器スイッチ刃部片Axは親スイッチ部片227の電源側の電分配導線225'に電氣的に接続してある。また電線225'は駆動スイッチ部片245の一方の側に電氣的に接続してある。スイッチ部片245の他方の側は継電器243のスイッチ接点d'に接続してある。駆動スイッチ部片には継電器242のスイッチ接点aと継電器243のスイッチ接点e'との間に電氣的に相互接続した

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駆動コイルを持つアムペライトバイメタルスイッチを備えている。紫外線灯冷却送風機電動機28は継電器243のスイッチ接点d', e'を横切りパイロットランプ28'に並列に接続してある。

継電器243のスイッチ刃部片Dxは継電器242のスイッチ接点bに600Ωの程度の定格を持つ抵抗単位247を介して電氣的に接続してある。スイッチ刃部片Cx, Exは継電器駆動ソレノイド243'の一方の側と共にスイッチ刃部片230の電源から遠い側の給電線231に電氣的に接続してある。ソレノイド243'の反対側は継電器242のスイッチ刃部片Bxに整流ダイオード249を介して電氣的に接続してある。250μF程度の容量を持つるべくは電解コンデンサ251は給電線231と継電器駆動ソレノイド243'の整流子接続端部との間に電氣的に接続してある。すなわちコンデンサ251はソレノイド243'に關係的に並列に接続してある。

変圧器240の1次巻線の一方の側は給電線231に1Ω程度の抵抗を持つ調整自在な抵抗器253を経て電氣的に接続してある。1次巻線の前記の側はまた継電器242のスイッチ接点b'に電氣的に接続してある。変圧器240の1次巻線の他方の側は継電器242のスイッチ接点a'に電氣的に接続してある。継電器駆動ソレノイド242'の一方の側はスイッチ刃部片230'の電源から離れた方の側の給電線231'に接続してある。ソレノイド242'の他方の側は継電器242のスイッチ接点e'とまた継電器243のスイッチ接点e'とに電氣的に接続してある。

本複写装置を動作に際して始動するようにスイッチ刃部片227を閉じるとカバー部片Cで制御するスイッチ刃部片CSが閉じているから継電器駆動ソレノイド242'が付勢状態になる。その理由はスイッチ刃部片Exがその協働する接点eに連関しているからである。そこで継電器スイッチ刃部片Ax, Bx, Cxをそれぞれ協働する接点a', b', c'に連関させると共にそれぞれスイッチ接点a, b, cとの電氣的接触をしや断する。

その結果スイッチ刃部片Cxとその協働する接点e'との連関によりスイッチ刃部片227, CSが閉じている限りはソレノイド242'を付勢状態に保持する。またスイッチ刃部片Axと接点a'との連関により給電線231, 225'の間の変圧器

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240の1次巻線と調整自在な抵抗器253とが直列に接続し従つて紫外線灯UVを変圧器240を介して動作するように付勢される。

送風機電動機28とそのパイロットランプとは可変抵抗器253の調整により制御される適定した遅れを置いて動作するように付勢され紫外線灯UVが適正な蒸気圧力に於て全負荷動作状態になるようにする。その理由は紫外線灯冷却送風機の作動が早過ぎると紫外線灯UV内に最速動作に必要な圧力条件が生じにくくなるからである。このためにスイッチ刃部片Bxとその協働する接点b'との電氣的連関によつて作動用ソレノイド243'が可変抵抗器253と並列でかつ変圧器240の1次巻線と直列な整流ダイオード249と直列になるようにしてある。従つてソレノイド243'は6V程度の電圧の整流電力により付勢される。この間にコンデンサ251はダイオード249からの電流によつて充電される。

コンデンサ251の充電が終つた後ソレノイド243'は継電器243を駆動するのに充分なだけ付勢されスイッチ刃部片Dx, Exをそれぞれ接点d', e'に電氣的に接続すると共に接点d, eから消勢された状態になる。スイッチ刃部片Exによる接点eの開放は、スイッチ刃部片Cxがその協働する接点e'に接触しているので付勢されたままになっているソレノイド242'に影響を及ぼさない。しかしスイッチ刃部片Dx, Exとそれぞれ協働する接点d', e'との連関により送風機電動機28とその協働するパイロットランプ28'との対向側部をそれぞれ抵抗器247およびスイッチ刃部片Dxを介してスイッチ接点bにまたスイッチ刃部片Dxを介して給電線231に接続する。この場合継電器ソレノイド242'が付勢されスイッチ刃部片Bxが接点bから離れているからスイッチ刃部片Dxと接点d'とが接触しても電動機28およびその協働するパイロットランプ28'の一方の側を継電器242の接点bに接続するだけであつてこの回路は開いたままである。

バイメタルスイッチ部片245を閉じたときにスイッチ部片245を介して給電線225'を接続するのは電動機28およびパイロットランプ28'の回路の前記のスイッチ刃部片Dxを介して給電線231に接続した側と同じ側である。バイメタルスイッチ部片245はその駆動ソレノイド

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を付勢したときに選定した時間遅れをおいてから開くようにした通常閉じた形式のものである。ところがさきに継電器242が駆動されてスイッチ刃部片Axが継電器接点aから離れているのでスイッチ部片245の駆動ソレノイドが消勢しているからスイッチ部片245は閉じ送風機電動機28とその駆動するパイロットランプ28'との一方の側は従つて給電線225'に接続する。従つて電動機28およびパイロットランプ28'は継電器243の駆動時に付勢され電動機28およびパイロットランプ28'の他方の側は接点e'およびスイッチ刃部片Exを介して給電線231に接続するようになる。紫外線灯冷却送風機はこのようにして紫外線灯UVに初期に動作エネルギーを加えてから或る時間遅れをおいて後始動する。このような遅れ時間は可変抵抗器253の調整抵抗値によつて定める。始動後に送風機電動機28は紫外線灯UVが動作するように付勢されている限りは作動を続ける。

本複写装置の作動は、スイッチ部片227を開くことによりまたはカバー部片Cをヒンジ部片Hのまわりに持ち上げてスイッチ部片C8を開いた場合にまたは回路保護装置すなわち電路しや断部片223, 223'等を作動することにより給電線の電力を止めた場合に止まる。このような場合にソレノイド242は消勢状態になりスイッチ刃部片Ax, Bx, Cxは継電器接点a, b, cに電気的に接続する位置に動くことにより接点a', b', c'との接続をしや断し減圧器240をスイッチ接点a'に於て電源から切りこれと同時に駆動スイッチ部片の作動ソレノイドにスイッチ接点aとこれに電気的に接触した刃部片Axとを経て給電線225'を接続する。またスイッチ部片245の作動ソレノイドの他方の側はスイッチ接点g'とこれに電気的に接触したスイッチ刃部片Exとを経て給電線231に接続する。従つて駆動スイッチ部片245は、スイッチ刃部片Axと接点aとの連関について或る選定した時間の経過後接点を開くようになりこのような時間の終りに送風機電動機28を止める。

継電器スイッチ部片242をその接点b'に於て開いてもそれによつて直ちに継電器ソレノイド243が消勢されるということはなくスイッチ部片242がその接点b'に於てこのように開いたこ

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とにより該ソレノイドに加わる整流電位がなくなるとソレノイド243を経てコンデンサ251が放電することになつて短い時間だけソレノイド243は付勢されたままになつてゐる。このような遅れ時間によりメイン刃部片Bxと接点bとの連関に回答して、1つのソレノイド付勢回路すなわち給電線225'からこの場合閉じている駆動スイッチ部片245と継電器スイッチ接点gと閉じた継電器スイッチ接点bを通る電圧降下用抵抗器247と整流ダイオード249と継電器ソレノイド243'とを経て給電線231まで延びる回路を形成することができる。このような回路は継電器ソレノイド243を紫外線灯冷却送風機電動機28およびその駆動するパイロットランプ28'を駆動スイッチ部片245がその付勢された駆動ソレノイドの影響のもとに開くまで動作状態に保つように付勢状態に保持するのはもちろんである。電動機28を前記のように時間遅れをおいて停止することにより紫外線灯UVが確実に冷却されて

紫外線灯UVをふたたび閉じた時にこの紫外線灯が迅速に始動できる単位までその内部の蒸気圧力を充分に下げることができる。この迅速な始動は紫外線灯UVがそのしや断後も温度が上昇したままになつてゐるとできないことである。電動機速度調整装置すなわち抵抗器229はハウジングの前壁Wに取付けた手動調整つまみ部片229'によつて作動できる。調整装置229の調整位置はつまみ部片229'に連絡した円板部片255により指示できる。円板部片255は前壁Wの前方に数字目盛付周縁部をこの周縁部に於て前壁Wに取付けた板部片257に形成した割出し記号に隣接した位置に於て露出させてある。円板部片255の目盛付周縁部または割出板或はこれ等四者は半透明の材料から作つてある。また電動機パイロットランプ71'を前記の半透明の部片の後側に取付け電動機71の作動を指示するようにしてある。送風機電動機用パイロットランプ28'は前壁Wに取付けた半透明の窓部片258の後側に取付けてある。

以上本発明を詳細に説明したが本発明の構成の具体例を要約すれば次のようである。

1. 制御装置を、通常閉じた時間遅れスイッチ部片と、このスイッチ部片を循環状態維持回路内に紫外線放出灯動作の終つたときに接続するよ

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うに動作して前記スイッチ部片が開くまで或る
時間だけ紫外線放出灯冷却媒質の循環を続ける
ようにする動作部片とにより構成した後記特許
請求の範囲に記載の複写装置。

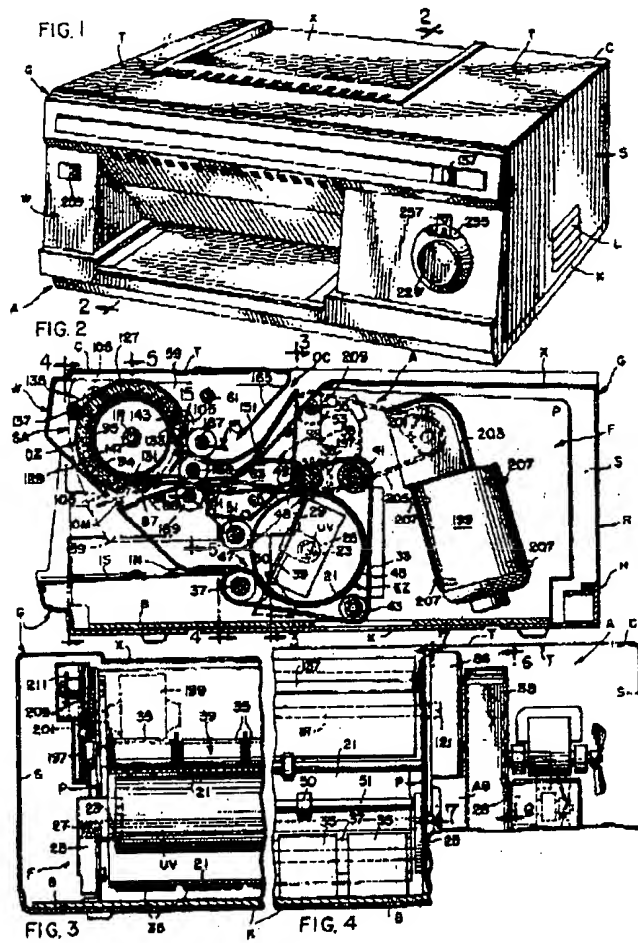
なお本発明はその精神を逸脱することなく種々
の变化変形を行い得るのもちろんである。

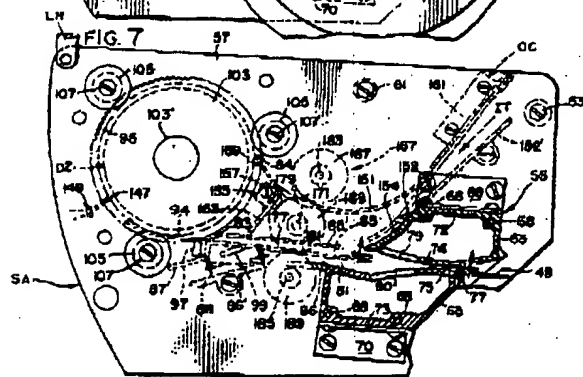
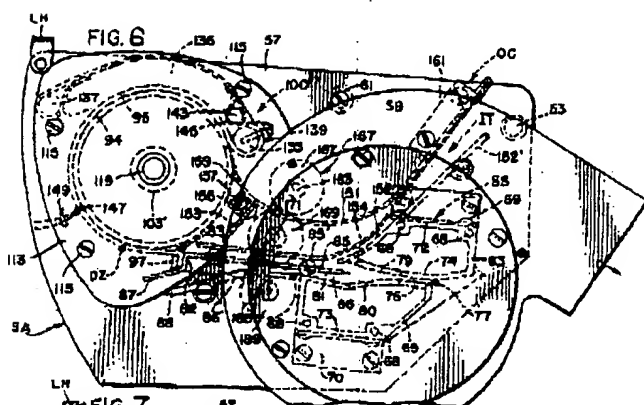
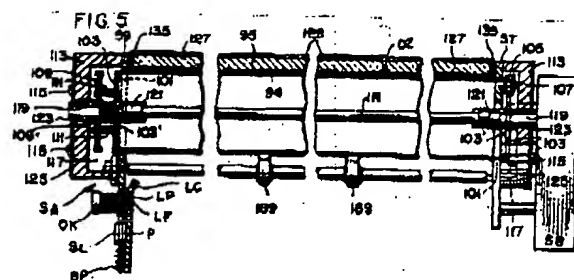
⑤特許請求の範囲

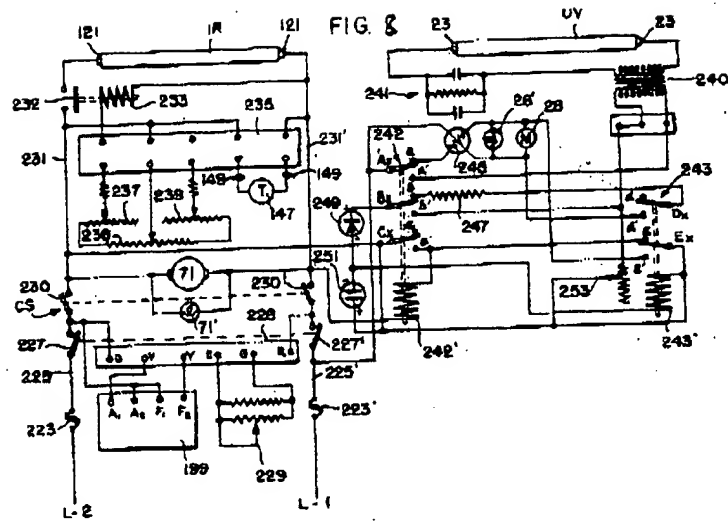
1 紫外線放出灯と、この放出灯を動作するよう
に付勢する電力を送る作用を持ち前記放出灯への
動作エネルギーの送出しを制御するスイッチ部片を
備えた回路と、前記放出灯に關係的に熱交換する
ように冷却媒質を循環させる作用をする作動部材
と、冷却媒質の循環を開始しまた停止する駆動コ
イルを持つ継電器、この継電器のコイルを付勢源

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からの切離し後或る遅れ時間だけ付勢状態に保つ
ように前記コイルに接続したコンデンサおよび紫
外線放出灯に動作エネルギーを送出す際に動作して
前記コンデンサおよびコイルにてコンデンサ充電
5 用および継電器コイル付勢用の電力を送る給電部
材を備え適当な付勢源から付勢されて前記放出灯
の始動後或る遅れ時間をおいて前記冷却媒質の循
環を始めさせこの循環を放出灯動作の終了後或る
時間だけ続けるようにする制御装置と、前記コイ
10 ルとこのコイルに接続したコンデンサとにこれら
両者の動作作用に一方の電力を送る整流部材と、
前記継電器コイル付勢回路内に接続され遅れ時間
を定める調整自在な可変抵抗器とを包含する、紫
外線の作用に材料を露出する複写装置。







TRANSLATION
JP-A-S48-6974

SPECIFICATION

1. Title of the Invention

Process of Decomposing Nitrogen Oxides and Apparatus Therefor

2. What Is Claimed Is:

1. A process of decomposing nitrogen oxides, characterized in that a dilute plasma of nitrogen oxides is formed and is contacted with a large area of heterogeneous catalyst support solids which do not undergo irreversible reactions with the components of said plasma.

2. A process of decomposing nitrogen oxides, which comprises passing a gaseous mixture containing a small amount of nitrogen oxides and a major amount of nitrogen through a thin discharge zone formed between electrodes connected to high voltage alternating current leads so as to establish a high voltage potential between the electrodes, the space between the electrodes containing a substantial amount of contact surface formed from particles of heterogeneous catalyst support solids which do not undergo irreversible reactions with the components of the gas, forming a low temperature plasma in the gas, and decomposing nitrogen oxides to nitrogen and oxygen.

3. A reactor for the removal of nitrogen oxides from a gas stream, characterized in that the reactor comprises a narrow and elongated chamber having inlet and exit ends, and a plurality of spaced apart electrodes disposed in said chamber, said space comprising a porous catalyst support material selected from alumina, magnesia,

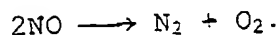
zirconia, silicate, aluminum silicate and mixtures thereof, said electrodes being connected to high voltage power leads and adapted to perform electric discharge for the formation of a dilute plasma.

3. Detailed Description of the Invention

The present invention concerns the decomposition of nitrogen oxides in plasmas in contact with surfaces which facilitate the decomposition.

Nitrogen oxides, especially NO, are common constituents of the exhaust gases issuing from hydrocarbon and coal combustion processes, examples of which include those of gasoline and other internal combustion engines, diesel engines, power plants, incinerators, etc. The exhaust gases from such processes commonly contain N_2 , CO_2 , and H_2O , along with lesser amounts of CO, H_2 , nitrogen oxides, unburned hydrocarbons, and oxygen. Among such constituents, nitrogen oxides, carbon monoxide, and unburned hydrocarbons are undesirable from an air pollution standpoint. There are various proposed ways of removing carbon monoxide and unburned hydrocarbons from exhaust gases, but it is proving difficult to find satisfactory and practical methods for removing nitrogen oxides from exhaust gases. It is advantageous to have a method of removal of nitrogen oxides which does not produce other undesirable pollutants or products. Depending upon location and relation to other pollution removal means, it may be desirable that the products do not cause problems with the means being used to remove hydrocarbons or other pollutants. It is also desirable that the means be a catalytic or similar means which does not involve a co-reactant which would be used up in the process, since many pollution control devices by their nature should be suitable for long term use without replenishment of components. Ideally, the removal of

nitrogen oxides would be accomplished by decomposition of NO involving only nitrogen and oxygen as products, e.g.,



In certain cases the oxygen produced via the decomposition may undergo secondary oxidation reactions. In general in the present invention the nitrogen oxides present in the exhaust are converted to molecular nitrogen as the principal nitrogen containing product. When the foregoing reaction is referred to in the present specification, it is to be understood that the oxygen may undergo secondary reactions.

It has been found that nitrogen oxides can be effectively decomposed to nitrogen and oxygen in a dilute discharge plasma in contact with surfaces of materials which are not consumed in the process. The materials involved have specific chemical and/or physical properties that make them effective in promoting the decomposition in the presence of dilute plasma. Some of the preferred solids exhibit maximum effectiveness when they have a relatively high specific surface area, but, some of the preferred solids give excellent results with relatively low specific surface areas.

In the procedure of the present invention, gases containing the nitrogen oxides are generally conducted through an electrical discharge zone containing solids (of appropriate material) presenting surfaces for the gases to contact. Generally such solids are a bed of solid particles in the form of spheres, cylinders, granules or other formed shapes, but various monolithic or other porous or reticulated structures permeable to gases can also be employed. The solids are preferably so disposed in the discharge zone that the gas being treated is simultaneously exposed to the discharge and to the solids. However it is within the broader aspects of the invention to separate the discharge and gas-solid contact, either in

time or location, and still obtain useful results from the utilization of both the discharge and the solids in the same process. The creation of a plasma in the gases, of course, does not depend upon the presence of the solids. The electrical discharge will be such as to provide a degree of ionization in the discharge zone sufficient to effect a marked decomposition of the nitrogen oxides under the conditions employed with a reasonable sized reaction zone and time. In practical use it is contemplated that the degree of ionization, power dissipation, and other conditions be such that a major portion of the nitrogen oxides are eliminated from the gas stream with accompanying conversion of the nitrogen oxides to nitrogen. In general to achieve good ionization conditions will require energy expenditures of at least 0.1 watt per cm^3 of reaction zone space, and more commonly at least 0.1 watt per cm^3 , while the expenditure is not apt to be over 200 watts per cm^3 , although there is no particular upper limit so long as there is not a break into a thermal arc under the conditions employed or inability to dissipate the heat generated with resulting excessive temperature conditions.

As is generally recognized, a plasma is an energetic gaseous mixture of ions and electrons (which can also contain excited neutral atoms, molecules and radicals). A dilute plasma is generally a non-self-sustaining discharge whose current-voltage characteristics are positive. A dilute plasma is characterized by relatively low electron currents, low gas kinetic temperatures, and it is generally true that the electrons and gas molecules are not in thermal equilibrium in a dilute plasma. For example, the gas kinetic temperature may be $100-500^\circ\text{C}$ while the electron temperature (as characterized by the kinetic energy of the electrons) may be greater than 5000°K . Such discharges require high externally applied

electric fields to accelerate the electrons to sufficiently high energy to ionize molecules and maintain the discharge. Common examples are direct current and alternating current corona, high pressure glow, radio frequency and microwave discharges. The degree of ionization for such plasmas depends upon the conditions of the discharge but is greater than would be expected from its gas kinetic temperature. An atmospheric pressure arc or self-sustaining thermal plasma is generally a highly ionized plasma, in which the molecules and electrons are essentially in thermal equilibrium with each other. It involves a discharge with negative current-voltage characteristic. Such a discharge is characterized by relatively high electron currents and gas kinetic temperatures between 5000° - $10,000^{\circ}$ K (See Gaseous Electrons, J. C. Cobine, Chapter 9, Dover Publications Inc., New York, 1958). Discharges involved in such arcs do not require large externally applied electric fields for their maintenance.

Ordinarily the type of plasma utilized herein, i.e., energetic gaseous mixtures of ions and electrons, is produced by an electrical discharge between a pair of electrodes which are separated from each other by at least one electrically insulating layer of dielectric such as glass or quartz, usually adjacent to or in contact with one of the electrodes. The discharge occurs between such electrodes of different potential which are separated by a gas. At a particular potential difference, depending upon the electrode distance, the gases present and other factors, there occurs a sharp increase in current flow between the electrodes to a value of the order of milliamperes, resulting from the electric field being strong enough to provide the naturally occurring electrons in the gas with sufficient energy to ionize neutral molecules upon collision. The current flow between

electrodes can be made to increase still further by increasing the voltage difference until a point is reached at which there would occur a sudden increase in current to the order of many amperes and a corresponding drop in voltage. The type of plasma produced under these conditions is much more highly ionized than that described and is generally called a high current arc or a thermal discharge. The discharges utilized herein generally involve relatively low currents (usually of the order of milliamperes per square centimeter of electrode surface or less) and relatively low degrees of ionization. The discharges include those commonly known as corona, glow, electrodeless and ozonizer discharges. The useful plasmas include dilute plasmas, which includes those sometimes termed cold and hybrid plasmas, which are essentially relatively low temperature media. Thermal arcs whose temperatures lie in the range of 5000° - $50,000^{\circ}$ K with kinetic energies of its constituent molecules, ions, and electrons being in equilibrium with the temperature are not generally suitable for the purposes of this invention. The gas kinetic temperatures of the plasmas employed herein generally range from ambient to hundreds of degrees, considered as an average of the temperature of the entire volume of gases involved. When oxygen is present, kinetics are such at excessively high temperatures that nitrogen and oxygen react to produce nitrogen oxides. In corona and ozonizer type discharges, and dilute plasmas in general, the degree of ionization is much greater than would be calculated from the gas kinetic temperature, and is maintained by the large electric fields present. The average temperature of the entire volume is still relatively low. The present process for the decomposition of NO is generally operated at gas kinetic temperatures of 0° - 1000° C or so, considering average temperatures as measured for example, by a

thermocouple in the reaction zone, or perhaps up to 1200°C or so allowing for the increase in the temperature of the gas mixture caused by the energy dissipated in the gas by the discharge. The temperature employed in practice will to some extent depend on the temperature of the exhaust stream involved, and this can to a large extent be varied by the position of the discharge zone in the exhaust train, or by the use of cooling or heating means. However, because of the kinetics of the decomposition reaction, and the high temperature properties of materials, it will not generally be desirable to exceed the stated temperature range by much, and the temperature should not exceed 2000-2500°C. While average temperatures are referred to herein, this contemplates an average of the gas volume where reaction is occurring, and not an average of a number of hot spots or thermal arc paths where thermal reactions occur at extremely high temperature, constituting the predominant reaction, while little reaction occurs in the balance of the reaction zone.

In general the present invention can use any type plasma which is effective to decompose NO to oxygen and nitrogen in the absence of oxygen and without employing high surface areas; and possibly extend the range of useful plasmas by the effectiveness of surfaces in facilitating the decomposition. The desired reaction will occur if a suitable plasma is employed, no matter how generated. In electrical discharges this is primarily by generation of electrons of the proper energy to ionize gas. Usually such electrons must have at least 9 to 11 electron volts, and possibly 15 electron volts or more. The methods of generation can include a modified corona discharge, a spark gap discharge (inductively coupled), a radio frequency discharge, microwave discharge, and combinations of the foregoing.

Some types of electrical precipitators involve

electrode wires of relatively small diameter separated by relatively great distances, and under the electrical conditions employed involve a small corona area around the wire and little or no ionization elsewhere. In such precipitators small solid particles are charged by electrons or ions in the gas and are then attracted to the charged electrode. They are removed by purely physical means, no chemical change or reaction having taken place. From a practical viewpoint an apparatus having such characteristics and employed in the usual manner (it involves power density of about 0.001 watt/cc.) would require an unreasonably long reaction zone to conduct a plasma reaction of the type involved here because of the presence of substantial volume where no reaction would occur, and because of the relatively low power density of such devices. Under the voltage and power density requirements of this invention, such precipitation devices would break down.

The apparatus employed in the exemplifications described herein employs electrodes separated by a gap containing gas subject to ionization. Considerable variation in the arrangement of the electrodes is possible, although there may be advantages in particular arrangements. The electrodes are generally employed with a considerable difference in AC potential, for example from 5000 to 40,000 or more volts with a particular embodiment described herein. Such potential will vary with the size and spacing of electrodes, resistance in the circuit, temperature, etc. A particular illustrated embodiment utilizes a dielectric (e.g. glass) wall between the electrodes as a resistance. Other electrical means can be employed to have inductance or impedance in the circuit which will serve as a resistance, but the nature of the discharge will then be altered from high pressure glow (modified corona) to a spark type discharge. For standard

corona disclosures alternating or direct current can be employed but alternating current is generally preferred for this invention because of the presence of the dielectric barrier between the electrodes. In general, the plasmas include any frequency from zero (direct current) up to microwave frequency and can be used with both low and high frequency. As the frequency changes, the electrode arrangement also must change, and in the case of radio frequency and microwave discharges, no central electrode is necessary. It will be recognized that plasmas are generated by a potential difference or electric field gradient in or across a zone containing gas to cause a discharge therein, rather than a potential gradient outside the gas containing zone. For example, if all the particles in the reaction zone were at the same dc potential, no discharge would occur since there would be no electric field gradient. The reactions desired herein do not depend upon or involve catalyzing or energizing gases, droplets or particles to an ignition point, nor involve combustion or burning of components.

It is also feasible to use a procedure in which the voltage is applied to the electrodes in intermittent manner or pulses, rather than continuously, thereby permitting a short time interval for ions or activated species to react before being subjected to further activating conditions. The gases can also be subjected intermittently to electric discharge conditions by being transported through spaced-apart zones where electrical discharge occurs. The use of voltage pulses has an advantage in the efficiency of power usage, although this is offset to some extent by the added cost of converting ordinary continuing voltage to such pulses.

The silent electric discharge reactor shown in the FIGURE includes a dielectric tubular pipe 1 containing a concentric inner electrode 2, and having mounted on its

outer surface a conductive covering 3 which together with the wall 4 of said pipe 1 forms an outer electrode assembly. The conductive covering 3 is connected to ground by lead 5. The inner electrode 2 is connected by lead 6 to the high voltage secondary of transformer 7 which is grounded by lead 8. The inner electrode 2 is insulatingly attached to the tubular pipe 1 by teflon gaskets 9 through which a side tube 10 is inserted to provide for exit of the gas stream. Sleeve 11 is of a dielectric material to prevent contact with the upper end of electrode 2. There is an inlet pipe 12 at the other end of tube 1, which is also fitted with a gasket 13 which can be of metal or dielectric material. The annular passage 14 between inner electrode 2 and wall 14 forms a discharge chamber in which packing materials 15 can be disposed. The packing material can be held in place by porous dielectric baffles 16 and 17, and below baffle 17 additional packing material 18 can be disposed which is generally of a different type than 15, although it can be the same. The reactor can be equipped with a jacket 19 for heating purposes. The exit pipe 10 is ordinarily connected to a sampling box which has appropriate valve means and side tube attachments for pressure reduction and forming a side stream which can then be analyzed in a quadropole mass spectrometer. The packing material 15 is generally a high surface area material or other type of material to facilitate the decomposition, while the material 18 is ordinarily only a contact material, e.g. ceramic spheres, for heat transfer purposes, although the same materials used for the 15 packing can be employed as the 18 material.

The illustrated apparatus can be used for a single pass of the gases through the discharge zone. However, if desired, it can be adapted for recycling part or all of the exit gases through the discharge zone or part thereof by recycling part or all of the exit gases to inlet pipe

12 or as a side feed at any point along pipe 1, either before or in the discharge zone. In the illustration the high voltage lead is to the inner electrode. The voltage leads can be reversed, but for operator safety it is preferred to have the high voltage on the inner electrode.

In general the plasma decomposition reaction in accordance with the present invention is ordinarily accomplished by passing the nitrogen oxide containing stream through a narrow elongated zone for plasma formation, such as for example the annular space between two concentric cylinders or tubes used as electrodes. The gap between the electrodes can vary widely, although generally distances no greater than 40 mm are employed, and can range down to less than 1 mm. The most suitable distances are generally in the range of 2 to 8 mm. The gap between the electrode contains materials as described herein. When the electrodes are metal as might be the case in a spark gap type discharge, the metal can be any metal generally used for electrodes. When the electrode employs a non-conductive surface, the surface can be glass, quartz, or other dielectric material, and various semiconductor materials can also be used. It is generally preferred that one of the electrodes be bare metal to lessen electrical resistance and increase power dissipation. Various sets, or a multiplicity of electrodes, can also be used. In the event that a pair of bare metal electrodes are used, the problems of arcing are increased, but this can be overcome by use of relatively large electrode spacing, evacuation of the discharge zone, by including resistance or inductance in the electric circuit, by arranging for solids to be present between the electrodes which are constantly in motion, and hence making and breaking electrical pathways, or suitable combinations of the foregoing. Various shapes and sizes of reactors can be used, employing various shapes and sizes

of electrodes, and the reactors can be arranged in horizontal, vertical or other direction and adapted for continuous or batch operation.

The mechanism of the reactions involved in the decomposition process of the present invention are not completely understood but are believed to involve some of the following:

I

1. $N_2 + \text{Discharge} \rightarrow N + N$
2. $NO + \text{discharge} \rightarrow NO^* \text{ (excited)}$
3. $NO^* + \text{Surface} \rightarrow NO \text{ (Adsorbed)}$
4. $N + NO(\text{Adsorbed}) \rightarrow N_2 + O(\text{adsorbed})$
5. $O \text{ (adsorbed)} + O \text{ (Adsorbed)} \rightarrow O_2 \text{ (adsorbed)}$
6. $O_2 \text{ (adsorbed)} \rightarrow O_2 \text{ desorbed}$

II

7. $N_2 + \text{Discharge} + \text{Surface} \rightarrow N + N$
8. $N + NO \rightarrow N_2 + O$
9. $O + O + M \rightarrow O_2 + M$

III

10. $N_2 + \text{discharge} \rightarrow N + N$
11. $NO + \text{discharge} \rightarrow NO^* \text{ (excited)}$
12. $NO^* + \text{Surface} \rightarrow NO \text{ (adsorbed)}$
13. $NO \text{ (adsorbed)} + NO \text{ (adsorbed)} \rightarrow N_2 + O_2 \text{ (adsorbed)}$
14. $N_2 \text{ adsorbed} + O_2 \text{ (adsorbed)} \rightarrow N_2 + O_2 \text{ (adsorbed)}$
15. $NO \text{ (adsorbed)} + NO^* \rightarrow N_2 + O_2$
16. $NO \text{ (adsorbed)} + N \rightarrow N_2 + O$

In the above reactions, N_2 is molecular nitrogen; O_2 is molecular oxygen; NO is nitrogen oxide; NO^* is excited nitrogen oxide; N is nitrogen atoms; O is oxygen atoms; and M is any third body.

In addition to the above cited reactions in various combinations it is also possible that under certain discharge conditions the reaction of the Nitrogen and Oxygen containing ions, radicals and excited molecules may occur at or near the surfaces to enhance the decomposition

of NO, and it is to be understood that the above reactions are not necessarily preferred or even required for the operation of the invention described herein. The role of the surface can be pictured as providing a template for adsorption of atoms and molecules and their subsequent reaction. Nitrogen apparently takes part in the reaction and it is considered advantageous to have nitrogen present during the discharge reaction. Generally nitrogen constitutes 50 to 80% or so by volume of the gases being treated to remove NO in accord with the present invention, and the procedure will, of course, work very well with up to 100% of the entering gas, other than nitrogen oxides, being nitrogen. Oxygen, of course, is involved in the decomposition process as one of the products, and its presence affects the reaction. Whenever possible, it is preferred for maximum effectiveness to keep the oxygen content to 3% or less by volume of the gases entering the reaction zone. The presence of higher amounts of oxygen has been found to be a problem in prior known procedures for decomposing nitrogen oxides. When oxygen concentrations of greater than 3% are present in combustion exhausts, it is one of the advantages of the present procedure that the use of suitable surface contact makes it possible to tolerate relatively high concentrations of oxygen, for example up to 5% by volume, and in the range of 5 to 12% by volume or so, and to obtain substantial decomposition of the nitrogen oxides, and even concentrations of oxygen up to the 20% or so found in air and higher and still obtain significant decomposition of nitrogen oxides under certain conditions. In general it is definitely advantageous to keep the oxygen content below 12%.

A wide variety of solids can be used for the contact surface in the present invention. However, the materials useful for such purposes in general have particular

characteristics in common. In general such surfaces are capable of some kind of interaction with NO or other gases in the gas stream. Many of the useful materials have relatively high specific surface areas, and a significant degree of porosity: By specific surface area is meant the surface area per gram as measured by the standard BET (Brunauer-Emmett-Teller) method using nitrogen as the adsorbate. Among the whole spectrum of materials which can be used, one finds materials having specific surface areas in the range of 0.01 to 800 square meters per gram. However, many of the efficient materials have specific surface areas of at least 5 square meters per gram. Since a surface phenomenon seems to be involved, it appears that some gas components are adsorbed on the surface, if only temporarily, for the reaction to occur. There are various ways in which gases can interact with a surface, including strictly physical adsorption, chemisorption, etc. Surface area is probably less significant in some types of interaction, e.g. possibly chemisorption, than in other types. Chemisorption can be defined as that type of adsorption in which there is rearrangement of electrons of the reacting gases and solids with formation of chemical bonds between the gas and solid surface; it can be regarded as a chemical reaction which is ordinarily restricted to the surface of the adsorbent. Physical adsorption is that adsorption caused by forces of molecular interaction which embrace permanent dipole, induced dipole, and quadrupole forces, and is the type of adsorption frequently referred to as van der Waals adsorption. The present procedure may involve both physical and chemisorption, as well as types of adsorption involving aspects of both of the foregoing as the gases go into or onto the solids.

In the examples herein, 70 grams of solids is representative of the amounts usually employed. At 0.01

square meters/gram specific surface area, this would be 0.7 square meter surface, and at 5 square meters/gram, would be 350 square meters, and 300 square meters/gram would be 21,000 square meters. Two liters/minute, and 6 liters/minute are representative of the gas flows used herein, and it can be seen that there is a wide variation in the total surface area of the solids that can be selected to treat such gas flows. This will be influenced by reactor design, temperature, discharge, etc. as well as the particular solid, but ordinarily at least half a square meter or so of surface of most solids would probably be involved in treatment of gas streams under the conditions illustrated herein.

In one particular aspect of the present invention, a dilute plasma is formed in a gas stream at ambient pressure, the gas stream containing nitrogen, no more than 5% by volume oxygen, and a small amount of NO, and decomposing the NO to nitrogen and oxygen. This can be done to some extent in the absence of the type of contact solids taught herein, provided the oxygen content is maintained below the stated value, but results are better with particular solids as taught herein.

In the procedures described herein, some of the gases may be more or less permanently retained in or on the solids. However, some temporary adsorption of gases may also be involved, and this may suffice for any surface interaction needed to effect the nitrogen oxides removal described herein. As used herein, "permanent adsorption" refers to a more or less irreversible retention of the gas on the solid, in the absence of some change such as heating to cause desorption, i.e., a type of retention in which the gas is not readily desorbed. "Temporary adsorption" is adsorption in which the gases are not permanently retained, but are readily desorbed. Materials of the type used herein may be capable of a certain degree

of adsorption even in the absence of plasma conditions. This type of adsorption is referred to herein as regular adsorption. For the most part, the regular, permanent adsorption by such materials of the gases of interest herein is negligible or very small, although such materials are operative even if such adsorption is present. The amount of regular, temporary adsorption is unknown, since it is difficult to measure, but may be fairly significant with some materials. Unexpectedly, in the present invention it has been found that a dilute plasma induces a significant amount of adsorption of gases by a number of materials. The adsorption of gases by materials in the presence of an electric discharge is referred to herein as induced adsorption. This induced adsorption phenomenon observed with NO is out of the ordinary in that it is observed only to a lesser degree or not at all with a number of other gases. The measured induced adsorption for the most part appears to be a permanent adsorption. The gases adsorbed (as determined by measurements on influent and effluent streams as described herein), appear to be retained on the surface indefinitely, unless the surfaces are heated or otherwise altered to cause desorption. As noted above, the amount of temporary adsorption is difficult to measure. However, the amount of temporary induced adsorption may be relatively large in the case of some of the materials employed herein. It will be noted that in some of the procedures herein the percentage adsorbed is reported separately from the percentage decomposed. If, in such cases, the decomposed material were adsorbed prior to decomposition, the true adsorption would be the sum of the decomposition and adsorption figures. Thus the adsorption figures herein are not always directly comparable, as more decomposition of NO was involved in some procedures than others. However, most of the materials utilized herein gave a

measured adsorption (not counting decomposition) of at least 0.0001 liters NO per minute, with about 75 cc. of the contact material, and employing a 2 liter/minute flow rate of a stream containing 0.15% NO, and a measured power dissipation of 80 watts, and some materials had adsorption rates better than 0.001 liters per minute under such conditions. It is to be noted that this adsorption is relatively independent of the NO concentration, within broad ranges of NO concentration. It should also be noted that the adsorption capacity of some of the materials is fairly large, as in some cases procedures have been run for weeks or a month at a time, with some fall off in NO removal, but still having substantial decomposition or adsorption after such times. Adsorption at a rate of 0.001 liter per minute for 30 days would result in adsorption of 43 liters of NO. In view of the relatively low concentrations of NO in exhaust gases, it can be seen that the described materials have an appreciable adsorption capacity with respect thereto. While there are advantages in use of materials with adsorption capability, some materials with only fair adsorption capability are better with respect to NO decomposition than some other materials of extremely high adsorption capability. Moreover, with some materials an electrical discharge does not induce a greater adsorption than would occur in the absence of such discharge, yet some such materials still show a good decomposition capability. As discussed herein, oxygen is one of the products of the decomposition reaction, and its presence in the effluent can be measured. However, it appears that oxygen may also be retained in or on the contact material to a varying extent. While the significance of this is not completely understood, there may be advantages in utilizing materials which permit the desorption or migration of such oxygen, if the presence of oxygen affects the availability of particular surfaces for

the NO decomposition.

The present process is not pressure dependent, although it will ordinarily be practiced at pressures within the range of 10 mm to 10 atmospheres. Ambient pressures are suitable. Pressure affects some types of electric discharge, and also affects the kinetics of some reactions, but the present process can be practiced over a broad range of pressures as stated.

In the present invention there are advantages in utilizing contact materials which are not consumed or burned in the reaction. Of course materials which react only in a catalytic sense, without any permanent or irreversible reaction, are not used up. Many of the materials utilized as contact materials herein are relatively inert so far as permanent chemical reaction is concerned, but aside from consumption of the material, such reactions are not necessarily disadvantageous. Some materials, such as carbon or other carbonaceous materials, can react or burn with generation of carbon monoxide or other undesirable concomitant products. Ideally the present invention produces nitrogen from nitrogen oxides and removes substantially all of the nitrogen oxides from a gas stream without substantial production of undesirable concomitant products.

The materials employed as surface contact material will generally have dielectric properties or be of no more than low conductivity. This is not necessarily an essential property, except to the extent necessary to avoid short circuiting when electric discharge means are utilized to produce the gaseous plasma. However, a number of the suitable materials are metal oxides or salts rather than the pure metals and accordingly of low conductivity. Where pure metals are used, they are generally dispersed on a dielectric surface so that the overall conductivity is still low, and the grains, granules, or other particle

forms are essentially non-conductive. Classes of materials which are generally suitable include the aluminum and silicon oxides, e.g., aluminas, silicas, aluminates, silicates, metal aluminum silicates, clays, molecular sieves, diatomaceous earths, etc., as well as similar materials from other materials in the same atomic groups. In general these materials will be employed in one of the forms in which heterogeneous catalysis supports are ordinarily employed in order to have contact with gaseous reactants, e.g. as particles, pellets, a porous structure, a fluidized bed, etc. Various other catalyst materials and the supports therefor will also be useful in the present procedure, although there will be considerable variation in their efficiency. For example, transition metals and metal oxides, including combinations thereof, can be used either dispersed on supports formed of porous particles of other metal oxides, or without dispersal on such supports, further specific examples of such materials including magnesia, thoria, zirconia, titania, hafnia, zirconium silicate etc. Various noble metals and their oxides can be employed, e.g., platinum, rhodium, and their oxides.

Nitrogen oxide containing gas streams were subjected to electric discharge in the reactor illustrated by the FIGURE, employing various packing materials. The reactor, as used in the following procedures had a 6 mm inner electrode 2, and the inner diameter of the dielectric pipe 1 was 17 mm, making a gap between the electrodes of approximately 5.5 mm. The outer ground 3 was about 32.5 cm in length, and the glow area extended about 2.5 cm on each end, making a total discharge zone about 37.5 cm in length. The volume in the grounded zone was about 75 cc, and about 95 cc for the total discharge zone. At a space velocity of 1300 reciprocal hours, there is a gas flow in the reaction of about 2 liters per minute, and at 4000 reciprocal hours, about 6 liters/minutes.

A 75 kilovolt transformer was used for the discharge, and the power expenditure in the secondary which was connected to the electrode was measured, and the input was regulated so this was generally in the range of 50 to 80 watts. However, there was considerable power loss in the high voltage cable to the electrode, and this was determined to be approximately half the input by measuring the power loss with open leads, so the power values reported in the procedures herein should be decreased by about one-half to approximate the actual power dissipation in the reactor itself. The current in the secondary was also measured at a point between the secondary and ground, and this also is adjusted in view of the losses in transmission to the reactor.

EXAMPLE 1

Utilizing a gas feed of 0.15% by volume NO, and the balance nitrogen, a discharge was run without external heating in the illustrated reactor at space velocity of 1300 hr^{-1} with a measured power loss in the secondary of 50 watts. The percentage of NO decomposed was 9.9%. At a measured 80 watts, the decomposition was 18%. When the flow rate was increased to correspond to a space velocity of 4000 hr^{-1} , 3.3% was decomposed at 50 watts, and 4.1% at 80 watts.

EXAMPLE 2

An approximately neutral alumina was used in the reactor, a total of about 80 cc of the material being used in the discharge zone. The alumina was essentially a gamma alumina. At a space velocity of 1300 hr^{-1} and measured power dissipation of 50 watts, with an approximate reactor temperature of 100°C , there was an NO decomposition of 19.7% when the entering stream contained 0.15% NO, with the balance Nitrogen. The NO was decomposed at the rate of

0.0061 liters/minute. There was also a permanent adsorption of 59% of the NO. When the measured power was changed to 80 watts, the decomposition was 31.1% and the adsorption 48.7%. At a space velocity of 4000 hr^{-1} , the decomposition was 6.3% at 50 watts, and 9.4% at 80 watts, with adsorptions of 31.8 and 30.9% respectively. The inlet stream was changed to include 1% oxygen, 1% carbon monoxide, and 10% carbon dioxide, and at a 4000 reciprocal hour flow rate, there was then a removal of 31.2% of the NO, 0.0029 liter being removed per minute. With a 1300^{-1} space velocity, the removal was 75.6%. The alumina (Al-0104-4) employed was further characterized by a total pore volume of 0.323 cc/gram, a macropore volume of 0.119 cc/gram, a surface area of 72 square meters/gram, and containing 0.19% Na. When an inlet stream was employed containing 0.2% NO, 5.0% oxygen, and the balance nitrogen, a 35% removal of NO was obtained at a space velocity of 400 hr^{-1} and measured power dissipation of 80 watts (from a 50 kV transformer) with an approximate temperature of 100°C . With an inlet containing 0.2% NO, there was a 40% decomposition of NO and 17% adsorption at 500°C , with a measured power dissipation of 80 watts (from a 50 KV transformer) at a velocity of 1900 per hour. Changing the power dissipation to 54 watts reduced the decomposition to 33.9%. When 1% oxygen, 1% CO, and 10% CO₂ were included in the gas, there was a 35.7% NO removal at measured power of 85 watts. With a 0.15% NO concentration and 80 watt power at 500°C , the NO decomposition was 22.8%.

In the above and other procedures, NO is adsorbed on the packing material, and this generally occurs to a greater extent than the decomposition. This can be monitored by measuring both the NO and the oxygen in the effluent stream, with the amount of NO decomposition being determined from the amount of oxygen produced. However, when oxygen is also present in the inlet stream, the

monitoring of oxygen production requires determination and allowance for a background value, and only the total NO removal is reported here. Ordinarily the actual decomposition can be approximated by determining the amount of NO adsorbed under the same conditions but in the absence of oxygen, and subtracting this value from the total NO removed. In the present procedures it would be preferred to decompose all the NO to nitrogen and oxygen. However, the adsorption of NO on the packing material does keep it from being present as a contaminant in the effluent, and will be a satisfactory method of removal so long as the NO is not readily re-emitted under conditions of use, and up to the time the packing material is saturated. Considering the small amount of NO in exhaust gases, and the fairly high adsorption capacity of some materials, it may be feasible to use materials depending partly on adsorption capacity for NO removal, and still have a sufficiently long life of the material for use as exchangeable cartridge in motor vehicles.

EXAMPLE 3

The illustrated reactor was packed with magnesia pellets and nitrogen gas at ambient pressure containing the specified amount of NO was passed through the reactor under discharge conditions with results as reported in the table.

Table I

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1300	100	0.15	50	12.7	70.1	
2	1300	100	0.15	80	47.3	36.1	
3	4000	100	0.15	50	11.7	21.3	
4	4000	100	0.15	80	17.6	19.8	
5	4000	100	0.15*	50	--	--	26.1
6	1300	100	0.15*	50	--	--	80.8

*Inlet gas also contains 1% oxygen, 1% CO, and 10% CO₂.

EXAMPLE 4

A macroporous silica with surface area of 120 square meters per gram was utilized in the illustrated reactor with nitrogen at ambient temperature carrying NO, with the following results:

Table II

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	4000	100	0.15	50	5.8	10.3	
2	4000	100	0.15	80	10.9	15.5	
3	1300	100	0.15	50	32.8	20.3	
4	1300	100	0.15	80	45.3	26.4	
5	1300	100	0.15*	50	--	--	23.2
6	4000	100	0.15*	50	--	--	16.1

*Gas also contained 1% oxygen, 1% CO and 10% CO₂.

The illustrated reactor was used with a packing of approximately 1/8 inch diameter aluminum oxide balls (Alumdum brand of pure, crystalline granular aluminum oxide), and with a quartz shielded inner electrode, and the outer tube being a heat and chemically resistant glass (Vycor) as usual. With a 1300 reciprocal hour flow rate of a stream containing 0.2% NO, and use of a 50 KV transformer to give approximately a 0.9 milliamper current in the secondary, there was a 9.3% decomposition of the NO, and 8% adsorption. The procedure was conducted without external heating, so the temperature in the reactor was approximately 100°C. When the temperature was raised to 300°C., there was a 22.2% removal of NO with approximately a 1.1 milliamper secondary current. At 250°C and 1465 hr⁻¹, there was 12.9 % NO decomposition and 45.3% adsorption at a 0.6 milliamper current. When the current was shut off, the overall NO removal dropped to 10.8%.

EXAMPLE 5

The illustrated reactor was packed with 95 cc of an alumina catalyst support, and 6 inches of granular aluminum oxide balls below such support. The aluminum oxide catalyst support (KA 201) had a surface area of about 230 m² /gram, and 67.8 grams was employed. Employing a nitrogen feed stream with a small amount of NO, results were as follows:

Table III

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1900	100	0.2	85	60.2	29.2	
2	1900	470	0.15	45	20.8	0	
3	1900	470	0.15	85	39.4	0	

EXAMPLE 6

The illustrated reactor was packed with 50 grams of an alumina catalyst support (Br 1570-02), 8×14 mesh, having an approximate 100 cc volume. With a nitrogen stream containing 0.2% NO, results were as follows:

Table IV

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	4000	100	0.2*	80	--	--	50
2	5000	100	0.2	80	20.8	32.3	
3	5000	100	0.2*	80			55

*Inlet stream also contained 1% O₂, 1% CO, and 10% CO₂.

EXAMPLE 7

A silica gel (Davison SG-59) was utilized in the illustrated reactor with a nitrogen stream containing a small amount of NO, with results as follows:

Table V

Proce- dure No.	Space Velocity hr ⁻¹	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1300	100	0.15	50	9.3	38.3	
2	1300	100	0.15	80	28.0	22.5	
3	4000	100	0.15	50	9.9	10.3	
4	4000	100	0.15	80	16.9	19.6	
5	4000	100	0.15*	50			13.2
6	1300	100	0.15*	50			32.8

*Inlet gas also contained 1% O₂, 1% CO, and 10% CO₂.

EXAMPLE 8

A silica alumina (Houdry, S-90) was utilized in the illustrated reactor, and gave an 18.9% decomposition and 33.5% adsorption, utilizing a nitrogen stream at 1300 hr⁻¹ and containing 0.15% NO with a measured power dissipation of 50 watts. The decomposition was 28% with 80 watt power. With a stream also containing 1% O₂, 1% CO, and 10% CO₂, the total NO removal was 33.6%.

EXAMPLE 9

The illustrated reactor was packed with a zirconium silicate support having a surface area of about 0.1 m² per gram. With a nitrogen stream containing a small amount of NO, results were as follows:

Table VI

Procs- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1300	100	0.15	50	75.6	12.2	
2	1300	100	0.15	80	79.6	16.9	
3	4000	100	0.15	50	34.5	18.2	
4	4000	100	0.15	80	61.5	12.3	
5	4000	100	0.15*	50			18.4
6	1300	100	0.15*	50			43.9

*Inlet stream also contained 1% O₂, 1% CO, and 10% CO₂.

EXAMPLE 10

A different zircon support was employed, with results as follows:

Table VII

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1300	100	0.15	50	47.4		
2	1300	100	0.15	80	68.2		
3	4000	100	0.15	50	10.4		
4	4000	100	0.15	80	16.8		
5	4000	100	0.15*	50			18.7
6	1300	100	0.15*	50			31.1

*Inlet stream also contained 1% O₂, 1% CO, and 10% CO₂.

Zirconium silicates as employed herein typically have an analysis, Al₂O₃, 2.97%; SiO₂ 32.33%; Fe₂O₃ 0.17%; and zirconium and hafnium oxides (mostly zirconium), 64%.

EXAMPLE 11

An acidic alumina (Engle hard RD-Al-3) of about 449 m²/gram surface area was employed in the discharge reactor, and gave a 15.5% decomposition and 79.5% adsorption of NO with a 50 watt measured power dissipation, at 1300 hr⁻¹ with 1% O₂, 1% CO, and 10% CO₂ also in the inlet stream, there was approximately 100% removal of the NO.

EXAMPLE 12

A molecular sieve material was placed in the reactor, a volume of 95 cc being used with weight of 58 grams. With a 4000 hr⁻¹ flow rate and 0.2 NO in nitrogen,

the decomposition at 80 watts measured on the secondary was about 55%. With 2% oxygen added, this changed to about 75%, and then was about 78% for 3 to 4% oxygen.

EXAMPLE 13

The reactor was packed with 85 cc of an alumina support (Al-0104-4), and used to remove NO from a nitrogen stream containing 0.2% NO. The NO decomposition was virtually complete at a 2 liter/minute flow and a measured current in the secondary of the 50 KV transformer of 4 to 5.6 milliamperes. When oxygen was added in concentration of 1%, 2%, 3% and 6.5% of the inlet stream, the NO removal was in the range of 95-100%. At 9.4% oxygen, the NO removal was about 70%, and at 12.4% oxygen, the NO removal was about 45%. (The analytical procedure differed from that of other examples).

When the reactor employed herein was packed with 95 cc. of silica catalyst support, 50 volts on the primary gave a measured 12 watts power on the secondary and 1.4 milliamperes current on the secondary. With the primary voltage at 100, the secondary measured 66 watts and 4.24 microamperes. These measurements were with no gas flow, but did not differ greatly from these with gas flow. With the reactor disconnected from the high voltage lead, a primary voltage of 55 resulted in a 7 watt power measurement in the secondary, with 4.1 milliamperes. Use of 105 volts on the primary gave a primary current of 1.7 amperes, power on the secondary of 21 watts, and current on the secondary of 6.8 watts. The foregoing illustrates that the shielded cable from the secondary to the high voltage electrode uses considerable power.

With some materials it was found that the plasma formation caused a great increase in adsorption capability, e.g. a neutral alumina (KA-201) of surface area about 230 m²/gram, absorbed much more NO in the

presence of the electric discharge. There can be advantages in using materials of such augmented adsorption characteristics in the present invention. The material decomposed 7.7% and adsorbed 33.9% of NO from a nitrogen stream at 50 watts and 4000 hr⁻¹.

EXAMPLE 14

Cobalt oxide was used as the packing in the reactor, and a 12.6% decomposition and 22.9% adsorption was obtained at 100°C, 1300 hr⁻¹ and 80 watts power.

EXAMPLE 15

When the reactor illustrated herein was packed with carbon, and nitrogen containing NO passed therethrough under discharge conditions, the NO removal was approximately the same as that obtained with no solid present. With 0.2% NO and 80 watts power, about 5% of the NO was removed at 4000 hr⁻¹. Carbon monoxide and carbon dioxide were observed in the effluent, and there was no oxygen observed when operating at about 500°C. At temperatures around 100°C, a very small amount of oxygen was produced, but the reaction products were predominantly carbon monoxide and carbon dioxide.

EXAMPLE 16

The illustrated reactor packed with high surface area alumina (KA-201) was utilized at 80 watts and 4000 hr⁻¹ to remove NO from a nitrogen stream containing 0.15% NO. At 100°C approximately one-third of the NO was removed, with about one-fifth of that removed being decomposed, as determined by the quantity of oxygen produced. The NO feed in the inlet stream was cut off, so that only nitrogen was being fed. The oxygen in the effluent dropped to a fraction of that previously determined, but was still a significant quantity. This

demonstrates that the NO was adsorbed, and that it was decomposed on the surface of the solid to produce the oxygen. .

EXAMPLE 17

The reactor was set up with approximately 90 cc. (65 grams) of high surface area alumina, and utilized with a 6 liter per minute nitrogen flow rate with 0.2% NO. The NO does not show significant permanent adsorption in the absence of discharge. With 50 watts power, the adsorption was originally about 0.004 liters/minute, and declined to about 0.0025 liters/minute at 30 minutes, and stayed near this value with only a gradual decline in the average value, for 90 minutes. The actual measured values fluctuated above and below this value when measured at time intervals. The discharge was stopped, and the NO measured in the effluent was then slightly greater than that in the feed stream. The nitrogen flow rate was changed to 2 liters per minute and the NO in the feed stream was turned off, and NO desorption was measured as the reactor temperature was raised by heating. The NO desorption varied widely between about 0.0003 liters per minute and 0.003 liters/minute, as the temperature was raised to about 300°C. at 80 minutes, and then to about 0.0058 liters/minute as the temperature was raised to over 400°C. The desorption rate generally responded to increases in temperature and then declined until the temperature was again increased. Oxygen in the effluent was determined as slightly over 0.0001 liters per minute at 50 minutes, approximately 0.0002 liters/minute at 90 minutes, and then rising to 0.0018 liters per minute at 102 minutes as the temperature reached about 480°C.

EXAMPLE 18

Gases were flowed through a 3/4 inch internal

diameter tube at pressures from 1 to 250 mm at space velocities ranging from 25 to 150 hr⁻¹. Microwave power was transmitted from a power supply to a tuned resonant cavity in the tube and the gas passing through the cavity was caused to discharge producing a dilute plasma over a 5 cc. volume discharge zone. Power densities ranging from 20 watts/cc to 500 watts/cc were used to obtain 30 to 50% decomposition of NO in a gas stream containing 0.2% NO. Similar decomposition is obtainable employing solid contact surfaces, such as aluminas, under conditions to avoid excessive heating. Radio frequencies can also be employed, e.g. those in the 100 kilocycle to 100 megacycle range.

Various metal oxides can be used as the solid contact material herein, some of which have been exemplified hereinabove, but there will be a wide variation in efficiency for nitrogen oxide decomposition as taught herein. Such oxides are in general catalysts for some oxidation reactions, but a number of them are often used in unsupported form, or as catalyst supports. Among such materials which can be used, and an example of a crystalline form for such use, are Cr₂O₃ (Corundum type), α -Fe₂O₃ (Hematite), NiO (Bunsenite), CuO (Tenorite), Co₃O₄ (Spinel type), Mn₂O₃ (Bixbyite), Mn₃O₄ (Hausmanite), ZnO (Zincite), Pb₃O₄ (Minium), MgO (Periclase), ThO₂ (Thorianite), CeO₂ (Fluorite type), Ag₂O (Cuprite type), V₂O₅, TiO₂ (Anatase), ZrO₂ (Fluorite type), WO₃, γ -Al₂O₃ (Spinel type), SiO₂ (Amorphous), etc. Of course, other crystalline forms can also be used. Pellets of an activated metal oxide are suitable for use herein, such as pellets of activated alumina, beryllia, thoria, magnesia, zincite or zirconia. As is well known in the art, the activated form of these oxides is prepared by the careful dehydration of a hydrated form of the oxide (such as the dehydration of alumina trihydrate at approximately 1000°F)

to produce a dehydrated form having a high specific surface area and large internal pore volume. Activated alumina is particularly suitable. The carrier or support can be impregnated with various actives known to be catalytically active for various reactions, and such impregnation may at times be advantageous in the presently claimed procedures. In addition various silicates can be employed herein, including those exemplified hereinabove, along with various other silicas and silicates. Pumice can be used, being a highly vesicular lava or rock composed of complex silicates of aluminum, potassium and sodium. The metal oxides can be used in various forms, e.g., aluminum oxides can be in the form of alumina, hydrated aluminas, or aluminates, and reference is made to Encyclopedia of Chemical Technology, Vol. I, pp. 640-645 (Interscience Publishers Inc., N.Y., Fourth Printing, 1961). As is well known calcination or heating often changes the crystalline form of metal oxides, and heating at about 900°C can produce the γ -alumina, while temperatures above 1000°C. produce α -alumina, and both forms can be used herein. In general most catalyst materials or supports therefor useful in hydrocarbon cracking or reformation reactions have some value in the presently claimed process. There are advantages in using incombustible solids or materials which are relatively inert insofar as any permanent chemical change or consumption in the reaction is concerned. Non-carbonaceous materials are advantageous since it is undesirable to have materials which react with NO or oxygen to produce carbon monoxide which is a pollutant.

In utilizing the contact materials herein, the materials will generally be formed into particles of sizes in the ranges of 1/32 to 1/8 inch or so, although other sizes can be employed, as well as other forms of porous material.

Among the contact materials which have been found useful in the present process are the following:

A neutral α - Al_2O_3 with intermediate surface area (Hashaw Al-0104);

A neutral α -alumina with high surface area and substantial macropore volume (Kaiser KA-201);

High porosity, low density, high purity silica gel (Davison Silica Gel 56-59);

Commercial magnesia support (high pH) (Harshaw Magnesia Mg-0601);

Typical cecidic cracking catalyst (Handry Silica Alumina S-90);

Acidic alumina (Englehard Alumina RD-Al);

High Macroporosity silica gel support (Houdry Macroporous Silica Beads, 9C3 catalyst);

High macroporosity, low surface area zirconium silicate (Norton Zircon 4054).

Additional properties of the supports are set forth in Table VIII below.

TABLE VIII DESCRIPTION AND PROPERTIES OF SUPPORTS

Support	Form	Surface Area m ² /g	Particle Density		True Density		Total Pore Vol.		Purity	Impurities Present
			g/cc	g/cc	g/cc	cc/g	cc/g	cc/g		
Harshaw Al-0104	1/8" tablets	80-100	1.57	3.45	0.28-0.33	0.119	99%Al ₂ O ₃	0.19%Na, <0.04%K 0.009%Cl		
Kaiser KA-201	5×8 mesh spheres	332	1.20	3.10	0.510	0.101	--	0.27%Na		
Davison Silica Gel	granules	239	--	--	1.15	0.048	99.7% SiO ₂	--		
S6-59	3-8 mesh		1.00							
Harshaw Magnesia	1/8" tablets	28	2.0	3.6	0.20	0.007	98% MgO	--		
Mg-0601			0.208							
Houdry Silica	4mm tablets	400-410	0.8	2.4	0.77	--	86%SiO ₂	0.1%Fe ₂ O ₃ -max. 0.2%N ₂ O -max.		
Alumina S-90							12%Al ₂ O ₃	low soda		
Engelhard Alumina	1/16" extrudate	449	1.18	3.12	0.528	0.147	--			
RD-AL										
Houdry Macroporous	~3-6 mm	140	0.82	2.25	0.776	0.134	>99%SiO ₂	<0.1%Al ₂ O ₃ <0.1%Fe ₂ O ₃ <0.1%Na ₂ O		
Silica Beads,	oblate spheres									
9C 3 catalyst										
Norton Zircon 4045	--	0.020	3.96	--	--	--	39.9%SiO ₂ 53.4%ZrO ₂ +HfO ₂	4.8%Al ₂ O ₃ 0.3%Fe ₂ O ₃ 0.5%TiO ₂ 0.1%CaO 0.2%Na ₂ O 0.8%K ₂ O		

*Macropore = pores with diameter of at least 700Å

Among the gases for which the process herein is useful are for example, exhaust gases containing up to about 0.5% NO, 0.5 to 2 or 3% oxygen, 5 to 15% water vapor, 5 to 15% carbon dioxide, 0.5 to 3% carbon monoxide, up to 1 to 2% hydrogen, various hydrocarbons in amounts of parts per million, e.g. up to 500 ppm, and nitrogen for substantially the balance, or various combinations of one or more of the foregoing along with nitrogen oxides and nitrogen. The present process is particularly suitable for treatment of exhaust gases from gasoline engines, i.e., automobile motors, and such exhaust gases generally have compositions in the above ranges.

EXAMPLE 19

A porous thoria material was used in the reactor under ambient conditions producing a temperature of about 100°C in the reactor, with the following results:

Table IX

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1377	100	0.15	50	21.1	60.2	81.3
2	1377	25	0.15	0	4.5	0	4.5
3	1377	100	0.15	80	25.8	69.8	95.6
4	4133	25	0.15	0	1.5	5.0	6.5
5	4133	100	0.15	50	10.5	38.7	49.2
6	4133	100	0.15	80	19.7	34.0	53.7
7	4570		0.15*	50			37.1
8	1520		0.15*	50			89.8

*Inlet gas also contains 1% oxygen and 10% CO₂.

The thoria used was a thorium oxide in the form of pellets formed by compressing and calcining thorium oxide powder.

EXAMPLE 20

Potassium hydroxide deposited on silica in a 1% amount thereof was utilized in the reactor with the following results:

Among the gases for which the process herein is useful are for example, exhaust gases containing up to about 0.5% NO, 0.5 to 2 or 3% oxygen, 5 to 15% water vapor, 5 to 15% carbon dioxide, 0.5 to 3% carbon monoxide, up to 1 to 2% hydrogen, various hydrocarbons in amounts of parts per million, e.g. up to 500 ppm, and nitrogen for substantially the balance, or various combinations of one or more of the foregoing along with nitrogen oxides and nitrogen. The present process is particularly suitable for treatment of exhaust gases from gasoline engines, i.e., automobile motors, and such exhaust gases generally have compositions in the above ranges.

EXAMPLE 19

A porous thoria material was used in the reactor under ambient conditions producing a temperature of about 100°C in the reactor, with the following results:

Table X

Proce- dure No.	Space Velocity hr-1	Temp. °C	% NO	Power Watts	decom- posed NO %	adsorbed NO %	total NO removal %
1	1300	100	0.15	50	43.6	45.7	89.3
2	3915	100	0.15	50	38.0	50.6	88.6
3	1450	100	0.15*	50			75.7

*Inlet gas also contains 1% oxygen, 1% CO, and 10% CO₂.

The hydroxide treated silica was prepared by depositing a 1% amount of KOH on a silica (Davison No. 5) having a specific surface area of 800 m²/gram, a pore volume of 0.43 cc/gram, and of -18 +50 mesh size. The potassium hydroxide utilized in the foregoing example is exemplary of metal hydroxides, e.g., alkali and alkaline earth metal hydroxides, which can be deposited on aluminas, magnesias, zirconias, silicates, aluminum or zirconium silicates, other zirconium compounds or other contact materials taught herein, and utilized in the processes and reactors of the present invention.

A number of different contact materials were used in the reactor to remove NO from a dilute nitrogen stream thereof at about 100°C, space velocity of about 4000 hr⁻¹, and power input of 40 watts, with results:

Table XI

Material	% Decomposition	% Adsorbtion
None	3.5	0
Alumina (KA 201-3)	7.7	34
Alumina (Al 104)	9.4	30
Alumina (Englehard)	11.9	58.5
Alumina (Br 1570)	23.6	49.4
Silica (Pyrex Beads)	14.3	10.3
Silica (SG 59)	16.9	19.6
Silica (Houdry Macro- porous)	10.9	15.5
Silica Alumina	11.2	12.6
Zirconium Silicate	61.5	12.3
PbO ₂ *	3.0	46.0
Activated Carbon	~3	~10
Cobalt Oxide	4.0	10.0
Thoria	19.7	34.4
H treated Mol Sieve	3.5	36.4
Na treated Mol Sieve	3.9	30.9
FeO (Shell 105)	2.0	25.9
FeO (Shell 205)	3.5	36.0
1% KOH on silica**	38.0	50.6

*The value reported for adsorbtion is that observed in the discharge after the natural adsorbtion has decreased to zero.

**50 watts power, high secondary current.

Described hereinafter are gist of the present invention and concrete examples of embodiments, which are all included in the embodiments of the invention as

referred to in the Patent Law Section 65ter.

1. A process of decomposing nitrogen oxides, characterized in that a dilute plasma of nitrogen oxides is formed and is contacted with a large area of heterogeneous catalyst support solids which do not undergo irreversible reactions with the components of said plasma.
2. A process of above item 1 in which the dilute plasma is created by a discharge with a power dissipation of at least 0.1 watts per 1 cc of reactor space.
3. A process of above item 1 in which the nitrogen oxides are in a gas stream containing more than 5% by volume oxygen and in which 0.5 to 3% of the oxygen are bonded as carbon monoxide and 0.5 to 15% of the oxygen are bonded as carbon dioxide.
4. A process of above item 1 in which the exhaust from an automobile motor is treated and in which the decomposition involves adsorption of nitrogen oxides on solids and desorption of nitrogen and oxygen from such solids.
5. A process of above item 1 in which chemisorption is involved, in which the solids are electrically non-conductive material, in which the active catalyst substance is alumina, magnesia, zirconia, silicate, aluminum silicate or a mixture thereof, in which the plasma passes through the reaction space at a space velocity of at least 500 per hours, and in which the surface of the solid catalyst has a surface temperature of not greater than 1000°C.
6. A reactor for the removal of nitrogen oxides from a gas stream, characterized in that the reactor comprises a narrow and elongated chamber having inlet and exit ends, and a plurality of spaced apart electrodes disposed in said chamber, said space comprising a porous catalyst support material selected from alumina, magnesia, zirconia, silicate, aluminum silicate and mixtures thereof, said electrodes being connected to high voltage

power leads and adapted to perform electric discharge for the formation of a dilute plasma.

7. A process of decomposing nitrogen oxides, which comprises passing a gaseous mixture containing a small amount of nitrogen oxides and a major amount of nitrogen through a thin discharge zone formed between electrodes connected to high voltage alternating current leads so as to establish a high voltage potential between the electrodes, the space between the electrodes containing a substantial amount of contact surface formed from particles of heterogeneous catalyst support solids which do not undergo irreversible reactions with the components of the gas, forming a low temperature plasma in the gas, and decomposing nitrogen oxides to nitrogen and oxygen.

4. Brief Description of the Drawing

The attached FIGURE is an illustration of an apparatus suitable for carrying out the decomposition process of the present invention.

- 1 dielectric tubular pipe
- 2 concentric inner electrode
- 3 conductive covering
- 4 tubular pipe wall
- 5,6 lead
- 7 transformer
- 8 teflon gasket
- 9 lead
- 10 side tube
- 11 sleeve
- 12 inlet pipe
- 13 gasket
- 14 annular passage
- 15,18 packing material
- 16,17 porous dielectric baffle
- 19 jacket